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# COWLEY THEORY OF LONG- RANGE ORDER IN $\beta$ -CuZn

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## Cowley Theory of Long-Range Order in $\beta$ -CuZn

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The Cowley theory is used to estimate the effect of nonstoichiometry on long-range order in  $\beta$ -CuZn alloys.

Accurate Ising-model calculations of the temperature dependence of long-range order in  $\beta$ -CuZn are available at the present only for the stoichiometric alloy.<sup>1,2</sup> To estimate the change in the long-range-order curve due to a departure from the stoichiometric composition, we have investigated the approximate theory of order developed<sup>3</sup> and revised<sup>4</sup> by Cowley. Although its thermodynamic formulation is not rigorous, we shall show that this theory does give a long-range-order curve for equiatomic  $\beta$ -CuZn in good agreement with Ising-model calculations except at the higher temperatures near  $T_c$ , and it can give the proper dependence on

composition in the limit of low temperatures, so we suggest that it should give a reasonable estimate of the effect of nonstoichiometry over much of the range of temperature below  $T_c$ .

Cowley did not give an expression for long-range order in nonstoichiometric alloys in his papers. Our equations for the  $\beta$ -CuZn alloys are derived from his initial paper<sup>3</sup> after changing one approximation, which appears equivalent to using a simple form of the revised approach of his later papers.<sup>4</sup> Cowley developed an expression for the free energy in terms of the Warren short-range-order parameters  $\alpha_i$ , which had been shown to have

the limiting values

$$\alpha_L = \pm (1 - \epsilon^2)S^2, \quad (1)$$

where  $S$  is the long-range-order parameter as defined by Cowley, the atomic fraction of Cu atoms in the alloy has been written as  $\frac{1}{2}(1 + \epsilon)$ , and the + sign is used for sites on the same sublattice as the origin and the - sign for sites on the other sublattice. Now, in minimizing the free energy for  $S \neq 0$ , we change his approximation that all the  $\alpha_i$  are independent variables, assuming, instead, that  $S^2$  is the independent variable and, ignoring local correlations, that  $\alpha_i \approx \alpha_L$  for all sites. The resulting equation, which combines terms from both sublattices, is easily manipulated to give

$$kT \ln \left\{ \frac{1 + (1 - \epsilon)^2 S^2}{1 - (1 - \epsilon)^2 S^2} \left[ \frac{1 + (1 - \epsilon)^2 S^2}{1 - (1 - \epsilon)^2 S^2} \right]^2 \frac{1 + (1 + \epsilon)^2 S^2}{1 - (1 + \epsilon)^2 S^2} \right\} \\ = 4(1 - \epsilon^2)S^2 [8V_1 - 6V_2 + 12V_3 \dots], \quad (2)$$

where  $V_i$  is the usual  $i$ th-neighbor interaction energy. Letting  $S \rightarrow 0$  as  $T \rightarrow T_c$ , one finds

$$kT_c = \frac{1}{2}(1 - \epsilon^2)[8V_1 - 6V_2 + 12V_3 \dots], \quad (3)$$

and Eq. (2) can be written

$$\ln \left\{ \frac{1 + (1 - \epsilon)^2 S^2}{1 - (1 - \epsilon)^2 S^2} \left[ \frac{1 + (1 - \epsilon)^2 S^2}{1 - (1 - \epsilon)^2 S^2} \right]^2 \frac{1 + (1 + \epsilon)^2 S^2}{1 - (1 + \epsilon)^2 S^2} \right\} \\ = 8S^2 \frac{T_c}{T}. \quad (4)$$

Equation (4) is the basic equation for long-range order in nonstoichiometric  $\beta$ -CuZn. It reduces properly to Cowley's equation for the equiatomic alloy,

$$\ln \left\{ \frac{1 + S^2}{1 - S^2} \right\} = 2S^2 \frac{T_c}{T} \quad (5)$$

when  $\epsilon = 0$ . It is symmetric in  $\epsilon$ , and as  $T \rightarrow 0$  it predicts the limiting value

$$S_0 = 1/(1 + |\epsilon|), \quad (6)$$

which is the maximum value that the parameter  $S$  can have in an alloy of that composition. As  $T \rightarrow T_c$  it gives the asymptotic relation

$$S = \frac{3^{1/4}}{(1 + 3\epsilon)^{1/4}} \left( \frac{T_c}{T} - 1 \right)^{1/4}, \quad (7)$$

which is only weakly dependent on  $\epsilon$ .

Let us first compare the long-range-order curve for the equiatomic alloy with the recent Ising-model

TABLE I. Comparison of the long-range-order parameters  $S(\epsilon)$  for equiatomic  $\beta$ -CuZn ( $\epsilon = 0.00$ ) and for the alloy with 52 at.% Cu ( $\epsilon = 0.04$ ).

$T/T_c$	$S(0, 00)$	$S(0, 04)$	$S(0, 04)/S(0, 00)$
0.4	0.9928	0.9615	0.9685
0.5	0.9785	0.9569	0.9800
0.6	0.9525	0.9425	0.9894
0.7	0.9103	0.9046	0.9937
0.8	0.8429	0.8393	0.9458
0.9	0.7249	0.7226	0.9969
1.0	0.0000	0.0000	0.9976

calculations of Essam and Fisher<sup>1</sup> and of Baker and Essam.<sup>2</sup> There clearly will be significant differences for temperatures near  $T_c$ , since the Cowley theory shows  $S$  varying as the reduced temperature raised to the power 0.25, while the two Ising calculations give exponents of 0.30 and 0.31. However, at lower temperatures the agreement is surprisingly good; the value of  $S$  from Eq. (5) agrees with that from the [10, 10] Padé approximant of Essam and Fisher to better than 1% for  $T/T_c \leq 0.84$ , and it agrees with the "compressible" model calculation of Baker and Essam to within 2.3% for all  $T/T_c \leq 0.95$ .

Now let us compare the long-range-order curve for an alloy containing 52 at.% Cu ( $\epsilon = 0.04$ ) with that for the equiatomic alloy to illustrate the predictions of Eq. (4). The values of the long-range-order parameter  $S(\epsilon)$  for these alloys and their ratio are given in Table I as a function of  $T/T_c$ . At low temperatures the long-range-order parameter for the nonstoichiometric alloy is appreciably smaller, but it is here also much less temperature dependent, so the effect of the nonstoichiometry decreases rapidly with increasing temperature and is an order of magnitude less near  $T_c$ . The effect of nonstoichiometry on the usual normalized order parameter  $S/S_0$  is then of the opposite sense; nonstoichiometry increases this parameter by an amount varying from zero at  $T = 0$  K to a maximum at  $T_c$ .

Finally, it is interesting to compare these predicted effects with the discrepancies observed between our recent experimental measurements<sup>5,6</sup> (on an alloy with 51.9 at.% Cu) and the Ising-model calculations. The effect is of the appropriate sign to bring the theory and experiment closer together, but, as Domb<sup>7</sup> has suggested, it is too small to account for the observed differences, which are approximately three times the predicted effects on  $S/S_0$  near  $T_c$ .

<sup>1</sup>J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1967).

<sup>2</sup>G. A. Baker and J. W. Essam, Phys. Rev. Letters **24**, 447 (1970).

<sup>3</sup>J. M. Cowley, Phys. Rev. 77, 669 (1950).

<sup>4</sup>J. M. Cowley, Phys. Rev. 120, 1648 (1960); 138, A1384 (1965).

<sup>5</sup>C. B. Walker and D. R. Chipman, in *Proceedings of the Battelle Colloquium on Critical Phenomena*, edited

by R. E. Mills, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), p. 289.

<sup>6</sup>D. R. Chipman and C. B. Walker, Phys. Rev. Letters 26, 233 (1971).

<sup>7</sup>C. Demb, in Discussion of Ref. 5.